Anonymous Referee #3

Received and published: 9 October 2020

The manuscript by Sanchez et al. "Measurement report: Cloud processes and the transport of biological emissions regulate Southern Ocean particle and cloud condensation nuclei concentrations" reports on particle and cloud condensation nuclei measurements around the Southern Ocean during the SOCRATES and the CAPRICORN- 2 campaigns. The measurements from SOCRATES were interpreted as a combination of high and low CN and CCN concentrations (four combinations) and linked to back trajectories and fitted with a course-mode fitting procedure to isolate the PMA contribution to CCN and CDNC. In parallel CCN measurements were conducted on-board a research vessel (during CAPRICORN-2). Overall the measurements are very interesting and novel and should be published as a measurement report. I do however find that the manuscript needs improvement in several aspects. In particular I miss information about measurement methods.

General comments

1. Title: I find that the title should be revised. I think that the use of the word regulates is too strong and not justified.

We have changed 'regulates' to 'affect'.

2. CCN measurements

(a) Is the miniature CCNc (mCCNc) used and described in more details in literature? Or is it a miniature custom-made version of the one described in Roberts and Nenes,
2005?

The minature CCNc is a custom-made version described by Roberts and Nenes 2005.

(b) Details on the supersaturation calibration procedures is missing (both the mCCNc and DMT CCNc). Could the authors elaborate on this (in the manuscript or in data repository) and give details on how they estimate the instruments supersaturation? (e.g. assumed water activity? type of calibration aerosol? drying conditions? Uncertainty related to reported supersaturation?). I find it valuable and useful that the data is available online. Nice that you estimate the uncertainty in the CCN number concentration.

The procedure for calibrating the miniature CCN counter is identical to the method described by Roberts and Nenes 2005. In summary, empirical calibrations are derived using monodisperse ammonium sulfate particles that are dried and then measured by the CCN counter and a CN counter to derive the activated fraction. Kohler theory is used to derive the supersaturation (assuming a water activity of 1.0). An instrument model, discussed in Roberts and Nenes (2005), showed a standard deviation in the supersaturation estimate of about +/-0.01%.

In the manuscript we have added the following statement to address the questions on CCN details:
"The miniature CCN counters are custom-made and operate with the same physical principles as described by Roberts and Nenes (2005). Empirical calibrations are derived using dried monodisperse ammonium sulfate particles that are measured by the CCN counter and a CN counter to derive the activated fraction. Kohler theory is used to derive the supersaturation (assuming a water activity of 1.0). An instrument model, discussed in Roberts and Nenes (2005) showed a standard deviation in the supersaturation estimate of about +/-0.01%."

(c) What caused the scanning mode mCCNc instrument to have problems during RF01-05? How is this reflected in the uncertainty?

During the first five research flights, the scanning CCN counter laser optical threshold was mistakenly set too high. Typically, the CCN counter is set to count particles that grow to over 1 micrometer in diameter. With the optical threshold elevated, the counting threshold was greater than 1 micrometer, causing the instrument to only count a fraction of the activated CCN, particularly at the lower supersaturations. Post-experiment lab calibrations corrected these measurements by applying a scaling factor between 1.0 to 1.6 as a function of supersaturation. The observed standard deviation (σ) in the scaling factor was less than 7% for all supersaturations and was included in the standard error (σ/√N) calculation.

(d) How dry was the air before entering the CCN counters?

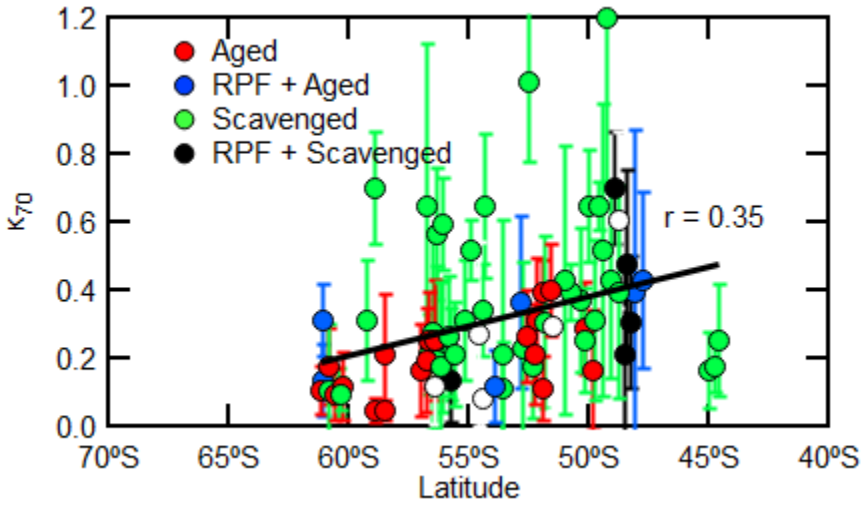
The air was dried before entering the CCN counter by heating in the inlet lines inside the GV cabin; however, that should not have any effect on the number of particles activated. Note that CCN calibrations are done using dry air (~ 40%). Anything more humid will not affect the results, and only drier air at the operating limits of the CCN (lowest supersaturation) could have a measurable impact.

3. Hygroscopicity Another major concern is related to the kappa parameter and hygroscopicity. Could the authors elaborate on how the _$_{70}$ was derived from scanning CCN spectra and UHSAS number size distributions? Did the authors estimate an kappa$_{70}$ uncertainty?

The text has been updated to better describe Kappa70:

> "The CCN spectra and UHSAS number concentrations on the GV were used to estimate the hygroscopicity parameter at 0.07 µm diameter (κ_{70}) for each MBL leg. For this calculation, the critical supersaturation is derived from the CCN spectra, where the UHSAS concentration at 0.07 µm diameter is equivalent to the CCN concentration."

The uncertainty (standard deviation) in the kappa value has been estimated and is now in figure 6d shown below.



L63: Could iodine new particle formation be a source in the SO? e.g. see the recent work of Baccarini et al. (2020) and Sipila et al. (2016).

Baccarini associates the NPF with increasing iodine during the transition from Arctic summer to autumn when the Arctic Ocean refreezes or ozone levels rise. Neither one of these conditions were observed during SOCRATES experiments. However, we cannot rule out the contribution of iodine emissions as a driver of NPF, particularly in the Antarctic coastal waters. No changes have been made to the text.

L101-103: "some studies suggest biologically productive waters enhance PMA production". Some studies show this relationship is not that simple. I suggest modifying the text to also reflect on this. See e.g. the work of Collins et al. (2016), Bates et al. (2020)

This sentence has been updated:

"Some studies suggest biologically productive waters enhance PMA production (Fuentes et al, 2010), while others suggest that biogenic content has little to no influence on PMA production (Collins et al., 2016; Bates et al., 2020). "

L108-110: "... can further reduce the hygroscopicity". A couple of studies also show that the hygroscopicity is not changing that much. I suggest the text to also reflect on this, e.g. see the recent work by Bates et al. (2020), Christiansen et al. (2020).
We have added the suggested citations to the discussion and have changed "can" to "may".

L170-172: Some details on aerosol inlet, sampling, calibration, data analysis or a reference to a paper/data repository giving these details is missing.

The following text has been added:

> "Details of the aerosol sampling system on board the RV Investigator are presented in Humphries et al. (2019) and Alroe et al., (2020). In short, aerosol sampling occurred via a common sampling inlet mounted on a mast at the bow of the ship, located 18 m above sea level. The CCN counter sampled from a manifold located 8 m below the mast in the ship's bow."
>
> "The full CCN data set collected on the RV Investigator during CAPRICORN2 are available at Humphries et al., (2020)."

L193: "UHSAS particles in the SOCRATES campaign were not fully dried". Could the author explain how this would affect the derived hygroscopicity parameter _?
After further discussion with instrument operators, we have concluded that the RH is expected to be reduced to less than 40% based on results from Strapp et al. (1992). Strapp et al. (1992) showed that the PCASP-100X dries aerosol almost completely (<40% RH) with the de-icing heaters. The UHSAS and PCASP are made by the same company (DMT) and have identical de-icing front ends. On a GV, there is additional heating related to ram air, consequently, we consider that the UHSAS air as completely dried (also < 40% RH). Despite this finding, we believe the PMA mode did not completely dry because of the presence of the 600 nm mode that correlates with wind speed. We hypothesize that the low residence time (~0.2 seconds) of the aerosol in the instrument prevented the larger hygroscopic sea salt from fully drying before being measured. This mode is only found in the MBL and not the FT, further suggesting its presence is a result of a deliquesced PMA mode. The deliquesced sea salt particles are not expected to affect the total UHSAS particle concentration, and therefore not affect the derived kappa parameter using the UHSAS lower cut off diameter of 70 nm.

We have updated the text to state

"PMA particles in the SOCRATES campaign were not fully dried"

We also added the following text:

"This deliquesced mode was present despite the findings by Strapp et al. (1992), suggesting the de-icing heaters of the PCASP-100X (which are identical to those used for the UHSAS) is expected to dry the particles to less than 40% relative humidity. We hypothesize that the low residence time of the aerosol in the instrument (~0.2 seconds) prevented the large hygroscopic sea salt from fully drying before being measured."

L200-204: A bit confused here: "The TEM analysis shows almost all particles >0.2 _m in diameter consist of sea salt; and sea salt particles account for 25% to 100% of particle number concentrations at particle diameters > 0.4 _m (Saliba et al. submitted)." How can almost all > 0.2 _m be sea salt, but not particles > 0.4 _m? How much is almost all? What kind of diameter is this (geometric, optical, mobility)? In addition, the title of the **Saliba et al. submitted** states "...in the North Atlantic". Was SOCRATES field campaign also in the North Atlantic?

This statement has been simplified to improve clarity:

"The TEM analysis showed that ~70-95% of marine boundary layer particles > 0.5 um optical diameter are PMA sea spray (Twohy et al. submitted)."

The previous version of this statement reference the wrong manuscript and should have referenced the manuscript listed below, which was a part of SOCRATES. However, the reference was changed to the more appropriate Twohy et al. submitted, which focused on the TEM analysis.

G. Saliba, K. J. Sanchez, L. M. Russell, C.H. Twohy, G.C. Roberts, S. Lewis, J. Dedrick, C.S. McCluskey, K. Moore, P.J. DeMott & D.W. Toohey (2020) Organic Composition of Three Different Size Ranges of Aerosol Particles over the Southern Ocean, Aerosol Science and Technology, DOI: 10.1080/02786826.2020.1845296

L212: Kernel density estimates. Interesting approach. Did you try k-means clustering analysis? If yes, how do they compare?

Yes, we tried a k-means clustering approach and the cases were categorized very similarly, and there were only a few differences at the thresholds between categories. We elected to use the kernel density approach as the visual showing the bimodality of the CN and UHSAS concentrations is more intuitive than the k-means clustering approach.

L232: The **Aged regime**: in addition, could aging be caused by atmospheric oxidants (OH ect.), e.g. changing chemical composition due to chemical reactions?

We absolutely believe aging is caused by atmospheric chemical reactions driven by oxidants. The text in the manuscript implies that ageing can also be caused by atmospheric oxidants:

The aged regime is "...likely due to atmospheric processes that increase particle size over time such as the condensation of VOC oxidation products or cloud processing."

L265: Sanchez et al., 2017. Still in discussion for ACP? Wrong citation.

The citation has been fixed.

L280: FT not defined I think.

We have now defined FT as free troposphere

L317: Would prefer to use **lower** _ instead of smaller _.
We agree and have changed “smaller kappa” to “lower kappa”.

L319-320: “... relative to sea salt (_ = 1.3)”. It has become clear that the hygroscopicity of NaCl and sea salt are not the same (Zieger et al., 2017; Christiansen et al., 2020) and that the _ value of sea salt _ 1 rather than 1.3. On a side note, Bates et al. (2020) writes about the CCN results in Quinn et al. (2014) that “It is critical to thoroughly dry the aerosol before it enters the CCN instrument. The SSA was not sufficiently dry during the WACSâˇARˇ 1 measurements”.
We agree that a hygroscopicity value of 1 is more representative of primary marine aerosol and have modified the text to indicate a value of 1.0 and cited Zieger et al. 2017 and Christiansen et al. 2020.

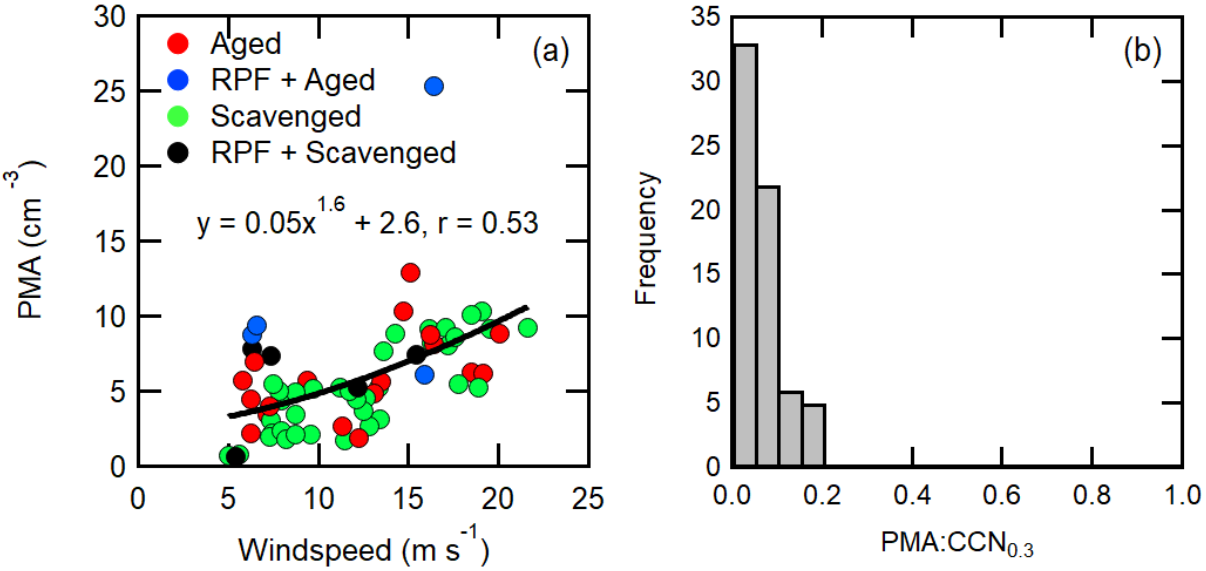
Regarding the comment about drying the air before it enters the CCN instrument, it is important to have dry classified aerosol (and correct for shape) when calibrating the CCN instruments. In Quinn et al. (2014), instrument setup was classifying the non-dry (deliquesced) SSA before sampling by the CCN and CN, which leads to incorrect calculation of solute mass for a given activation diameter – this has nothing to do with the operation of the CCN instrument. Once a CCN instrument is properly calibrated, one does not need to dry the aerosol. Caveat: The only condition where a measurable impact could occur is when operating the CCN instrument close to its low supersaturation limit in an environment significantly dryer than it was calibrated. In such a case, there is a small delay in the establishment of the peak supersaturation inside the column, which can reduce the residence time of droplet growth and lead to the undercounting of the activated aerosol particles.

L333: “...phytoplankton emissions...”. To help the reader, please be more specific here on what type of emission.
We have modified the text based on the comments from reviewer 2 and 3:

> “There are also elevated CCN concentrations north of 50°S measured on the R/V Investigator, probably related to continental emissions from Australia, elevated biomass emissions of VOCs (aerosol precursors), as suggested by increasing chlorophyll-a concentrations north of the subantarctic front (McCoy et al. 2015), and even long-range transport of Antarctic coastal emissions (Ayers and Gillett, 2000; Twohy et al., submitted).”

L347-348: “The calculated PMA number concentrations moderately correlated to wind speed (r = 0.53, Figure 6a)”. This is interesting. Why did you use a linear fit here?

The relationship between PMA and wind speed is non-linear (i.e., Grythe et al. ACP, 2014), and we have changed the linear fit to a polynomial fit. The r value remains 0.53.



L447-448: I can not find the processed CCN data for CAPRICORN-2 / RV Investigator through the provided link.

The link has been updated and works.

References:

Baccarini, A., Karlsson, L., Dommen, J. et al. Frequent new particle formation over the high Arctic pack ice by enhanced iodine emissions. Nat Commun 11, 4924 (2020). https://doi.org/10.1038/s41467-020-18551-0

Sipilä, M., Sarnela, N., Jokinen, T. et al. Molecular-scale evidence of aerosol particle formation via sequential addition of HIO3. Nature 537, 532–534 (2016). https://doi.org/10.1038/nature19314

Bates, T. S., Quinn, P. K., Coffman, D. J., Johnson, J. E., Upchurch, L., Saliba, G., : : : Behrenfeld, M. J. (2020). Variability in Marine Plankton Ecosystems Are Not Observed in Freshly Emitted Sea Spray Aerosol Over the North Atlantic Ocean. Geophysical Research Letters, 47(1). https://doi.org/10.1029/2019GL085938 Christiansen, S., Ickes, L., Bulatovic, I., Leck, C., Murray, B. J., Bertram, A. K., : : : Bilde, M. (2020). Influence of Arctic microlayers and algal cultures on sea spray hygroscopicity and the possible implications for mixedâ˘ARˇ phase clouds. Journal of Geophysical Research: Atmospheres, 125(19). https://doi.org/10.1029/2020jd032808

Collins, D. B., Bertram, T. H., Sultana, C. M., Lee, C., Axson, J. L., Prather, K. A. (2016). Phytoplankton blooms weakly influence the cloud forming ability of sea spray aerosol. Geophysical Research Letters, 43(18), 9975–9983. https://doi.org/10.1002/2016GL069922

Zieger, P., Väisänen, O., Corbin, J. C., Partridge, D. G., Bastelberger, S., Mousavi-Fard, M., : : : Salter, M. E. (2017). Revising the hygroscopicity of inorganic sea salt particles. Nature Communications, 8, ncomms15883. https://doi.org/10.1038/ncomms15883

Technical corrections

Overall, there are quite many mistakes in the reference list. This gives the reader a bad impression. The authors should solve this issue.

There were some errors when importing documents into the reference manager that were not changed before submission. We thank the reviewer for taking the time to point these out.

L452: Remove uppercase “AEROSOLS, CLOUD MICROPHYSICS, AND FRACTIONAL CLOUDINESS”

L463: Replace + with page number 363. “359-+,”
L467: What journal? Only says “aerosols, , (November), 1–27”. No DOI.
L470: Remove uppercase “SEASONAL RELATIONSHIP BETWEEN CLOUD CONDENSATION NUCLEI AND AEROSOL METHANESULFONATE IN MARINE AIR”
L495: Fix “67-+,”
L517: Remove uppercase “NEW PARTICLE FORMATION IN THE MARINE BOUNDARY-LAYER,”
L634: Is the * supposed to be there? “...Low Cloud Feedback*”
L670: ?? “Available from: %3CGo,”
L674: Make lowercase
L681: Make lowercase
L701: Remove symbol
L735: Who is “O'”. Maybe cite the final paper.
L742: Make lowercase
L757: No title??? What journal?
L801: Make lowercase
L808: Make lowercase

Table 1: _ what?
The authors do not understand this last comment.